

## Solutions:

HW#6

3.19. 3.21. 3.23. 3.33. 3.34. 5.8. 5.12. 6.48.

$$\begin{aligned} 3.19. \quad \frac{1}{T} &= -\frac{k}{2\mu_B} \frac{d}{dN_{\uparrow}} [N \ln N - N_{\uparrow} \ln N_{\uparrow} - (N - N_{\uparrow}) \ln (N - N_{\uparrow})] \\ &= -\frac{k}{2\mu_B} \left[ -\ln N_{\uparrow} - \frac{N_{\uparrow}}{N_{\uparrow}} + \ln (N - N_{\uparrow}) + \frac{N - N_{\uparrow}}{N - N_{\uparrow}} \right] = \frac{k}{2\mu_B} \ln \frac{N_{\uparrow}}{N - N_{\uparrow}} \end{aligned}$$

From (3.25)  $N_{\uparrow} = N/2 - U/2\mu_B$  so

$$\frac{1}{T} = \frac{k}{2\mu_B} \ln \left( \frac{N - U/\mu_B}{N + U/\mu_B} \right)$$

$$\frac{N - U/\mu_B}{N + U/\mu_B} = e^{2\mu_B/kT}$$

$$U = N\mu_B \left( \frac{1 - e^{2\mu_B/kT}}{1 + e^{2\mu_B/kT}} \right) = N\mu_B \left( \frac{e^{-\mu_B/kT} - e^{\mu_B/kT}}{e^{-\mu_B/kT} + e^{\mu_B/kT}} \right) = -N\mu_B \tanh\left(\frac{\mu_B}{kT}\right)$$

Recall  $\frac{d}{dx} \tanh x = \frac{1}{\cosh^2 x}$

$$\begin{aligned} C_B &= \frac{\partial U}{\partial T} = -N\mu_B \frac{1}{\cosh^2(\mu_B/kT)} \left( \frac{\mu_B}{k} \right) (-T^{-2}) \\ &= NK \frac{(\mu_B/kT)^2}{\cosh^2(\mu_B/kT)} \end{aligned}$$

3.21

$$\frac{\mu_B}{kT} = \frac{(5 \times 10^{-8} \text{ eV/T}) (0.63 \text{ T})}{(8.617 \times 10^{-5} \text{ eV/K}) (300 \text{ K})} = 1.22 \times 10^{-6}$$

$$\frac{M}{N\mu} = \frac{\mu_B}{kT} = 1.22 \times 10^{-6}$$

$$\frac{M}{N} = (1.22 \times 10^{-6}) (5 \times 10^{-8} \text{ eV/T}) = 6.1 \times 10^{-14} \text{ eV/T}$$

The energy difference between the two states

$$\epsilon = 2\mu_B = 63 \times 10^{-8} \text{ eV}$$

The photon with the energy has the wavelength

$$\lambda = \frac{hc}{\epsilon} = 19.7 \text{ meter}$$

3.23

$$\frac{S}{k} = N \ln N - N_{\uparrow} \ln N_{\uparrow} - N_{\downarrow} \ln N_{\downarrow}$$

$$N_{\uparrow} = \frac{1}{2} \left( N - \frac{U}{\mu_B} \right)$$

$$N_{\downarrow} = N - N_{\uparrow} = \frac{1}{2} \left( N + \frac{U}{\mu_B} \right)$$

Recall  $\frac{U}{\mu_B} = -N \tanh x$  where  $x = \frac{\mu_B}{kT}$

$$N_{\uparrow} = \frac{N}{2} (1 + \tanh x) = \frac{N e^x}{2 \cosh x}$$

$$N_{\downarrow} = \frac{N}{2} (1 - \tanh x) = \frac{N e^{-x}}{2 \cosh x}$$

$$\frac{S}{kN} = \ln N - \frac{e^x}{2 \cosh x} \ln \left( \frac{N e^x}{2 \cosh x} \right) - \frac{e^{-x}}{2 \cosh x} \ln \left( \frac{N e^{-x}}{2 \cosh x} \right)$$

$$= -x \left( \frac{e^x - e^{-x}}{2 \cosh x} \right) + \left( \frac{e^x + e^{-x}}{2 \cosh x} \right) \ln(2 \cosh x)$$

$$= \ln(2 \cosh x) - x \tanh x$$

3.33 For constant-volume process  $dU = Tds$

$$8/8 \quad C_v = \left( \frac{\partial U}{\partial T} \right)_V = T \left( \frac{\partial S}{\partial T} \right)_V$$

Enthalpy  $H$

$$H = U + pV$$

$$dH = dU + d(pV) = Tds + Vdp$$

$$C_p = \left( \frac{\partial H}{\partial T} \right)_P = T \left( \frac{\partial S}{\partial T} \right)_P$$

3.34 a) Multiplicity  $\Omega = \binom{N}{N_R}$   
14/14 2

Similar to magnetism

$$\frac{S}{k} = N \ln N - N_R \ln N_R - (N - N_R) \ln (N - N_R)$$

$$\sim b) L = \ell(N_R - N_L) = \ell(2N_R - N) \Rightarrow N_R = \frac{1}{2} \left( \frac{L}{\ell} + N \right)$$

$$\sim c) dU = Tds + FdL$$

$$d) dU = 0$$

$$\sim FdL = -Tds \Rightarrow F = -T \left( \frac{\partial S}{\partial L} \right)_U$$

$$\frac{\partial S}{\partial L} = \frac{\partial S}{\partial N_R} \frac{\partial N_R}{\partial L} = \frac{\partial S}{\partial N_R} \cdot \frac{1}{2\ell}$$

$$\text{So } F = -T \left( \frac{\partial S}{\partial L} \right)$$

$$= -\frac{kT}{2\ell} \left[ -\ln N_R - \frac{N_R}{N_R} + \ln(N - N_R) + \frac{N - N_R}{N - N_R} \right]$$

$$= -\frac{kT}{2\ell} \ln \left( \frac{N - N_R}{N_R} \right)$$

$$= \frac{kT}{2\ell} \ln \left( \frac{1 + L/N\ell}{1 - L/N\ell} \right)$$

e) When  $L \ll Nl$

$$\sim \frac{1 + L/Nl}{1 - L/Nl} \approx 1 + \frac{2L}{Nl}$$

$$\Rightarrow F \approx \frac{kT}{2l} \cdot \frac{2L}{Nl} = \frac{kTL}{Nl^2}$$

f)

$$F \propto T \Rightarrow T \uparrow \quad F \uparrow$$

$\sim$

For given  $F$ , increase  $T$  will cause  $L$  decrease to compensate. Because at higher temperature, there is more randomness in the orientation of the links, causing the rubber band to contract.

g) Under adiabatic stretching, the total entropy of the

$\sim$  rubber band should be constant. Stretching the band decrease the configuration entropy, so the temperature should increase to compensate. (Increase the kinetic entropy)

3.8

$$\begin{aligned}dG &= d(U - TS + PV) \\&= Tds - PdV + \mu dN - Tds - SdT + PdV + VdP \\&= -SdT + VdP + \mu dN\end{aligned}$$

If  $dN=0$   $dP=0$

$$dG = -SdT \quad \text{i.e.} \quad \left(\frac{\partial G}{\partial T}\right)_{N,P} = -S$$

Similarly,

$$\left(\frac{\partial G}{\partial P}\right)_{N,T} = V$$

$$\left(\frac{\partial G}{\partial N}\right)_{T,P} = \mu$$

5.12 Assume we have the system which

$$\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S}\right)_V = \frac{\partial}{\partial S} \left(\frac{\partial U}{\partial V}\right)_S$$

From  $dU = Tds - PdV$

$$\Rightarrow \left(\frac{\partial U}{\partial S}\right)_V = T \quad \& \quad \left(\frac{\partial U}{\partial V}\right)_S = -P$$

So we get first Maxwell equation

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

From  $dH = Tds + VdP$

$$\frac{\partial}{\partial P} \left( \frac{\partial H}{\partial S} \right) = \frac{\partial}{\partial S} \left( \frac{\partial H}{\partial P} \right)$$

$$\left( \frac{\partial T}{\partial P} \right)_S = \left( \frac{\partial V}{\partial S} \right)_P$$

From  $dF = -SdT - PdV$

$$\frac{\partial}{\partial V} \left( \frac{\partial F}{\partial T} \right) = \frac{\partial}{\partial T} \left( \frac{\partial F}{\partial V} \right)$$

$$\left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V$$

From  $dG = -SdT + VdP$

$$\frac{\partial}{\partial T} \left( \frac{\partial G}{\partial P} \right) = \frac{\partial}{\partial P} \left( \frac{\partial G}{\partial T} \right)$$

$$\left( \frac{\partial V}{\partial T} \right)_P = - \left( \frac{\partial S}{\partial P} \right)_T$$

6.48

a) The internal contribution to the free energy is

$$F_{int} = -NKT \ln(Z_e Z_{rot})$$

$$Z_{rot} = \frac{kT}{\epsilon} \text{ or } \frac{kT}{2\epsilon} \text{ at ordinary temperature. (see (6.31) \& (6.33))}$$

$$\frac{\partial F_{int}}{\partial T} = -NK \ln(Z_e Z_{rot}) - NK T \cdot \frac{1}{T}$$

(6.92)

$$S = NK \left[ \ln \left( \frac{V}{Nv_0} \right) + \frac{5}{2} \right] + NK \left[ \ln(Z_e Z_{rot}) + 1 \right]$$

$$= NK \left[ \ln \left( \frac{V Z_e Z_{rot}}{Nv_0} \right) + \frac{7}{2} \right]$$

The rotational partition function for oxygen at room temperature is

$$Z_{\text{rot}} = \frac{kT}{2\epsilon} = \frac{18.617^{-5} \text{ eV/K} (298 \text{ K})}{2 \cdot (0.00018 \text{ eV})} = 71$$

While the eqn.

$$v_Q = \left( \frac{h}{\sqrt{2\pi m k T}} \right)^3 = 5.73 \times 10^{-33} \text{ m}^3$$

the average volume per particle is

$$\frac{V}{N} = \frac{kT}{P} = 4.07 \times 10^{-26} \text{ m}^3$$

$$\ln \left( \frac{V}{N} z_e \frac{Z_{\text{rot}}}{v_Q} \right) = 21.14$$

$$S = Nk [21.14 + 3.50]$$

$$= 24.6 NR = 205 \text{ J/K}$$

b) The chemical potential is  $-kT$  times the same logarithm:

$$\mu = -18.62 \times 10^{-5} \text{ eV/K} \cdot (298 \text{ K}) (21.14) = -0.54 \text{ eV}$$